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PRODUCTS OF PHOTODEGRADATION FOR COUMARIN LASER DYES
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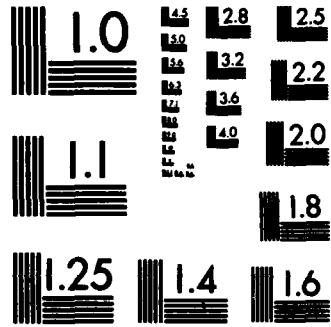
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52

PRODUCTS OF PHOTODEGRADATION FOR COUMARIN LASER DYES

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Abstract

The products of conventional photolysis of the coumarin laser dyes, C1, C35, C153, and C152 have been investigated. The previously reported dealkylation of C1 is documented for the fluorinated dyes, C35, and C152 in deaerated solvents. In addition, a reduction product is identified for C1, consistent with a radical mechanism for decomposition. Evidence is provided that the concentration quenching (self quenching) of singlet dye is important to the degradation mechanism. For the rigid dye, C153, a photooxidation product involving the amine functionality results from decomposition in aerated media. For several dyes, very low triplet yields have been measured.

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The stability of coumarin dyes during dye laser operation has been of interest for some years.^{1,2} The effects of medium, cover gas, dye structure, and optical filters have been investigated extensively.³ Quantum efficiencies for photodecomposition have been reported in rare cases,^{3,4} and the effects of additives which improve performance under lasing conditions have been documented.⁵ The products of photodegradation for a single coumarin dye have been identified in the early report of Winters, Mandelberg, and Mohr.⁶ We wish to establish that the dealkylation process noted by the latter authors for C1 is also important for other related dyes. Furthermore, another type of product accompanying dealkylation and characteristic of radical disproportionation has been identified for C1. In addition, the decomposition of a dye having a "rigid" structure (C153), which is known for its stability,⁷ has also been investigated.

Product studies. Dyes chosen for study are the 7-aminocoumarins shown below which are commercially available ("laser grade") from Eastman (Cxx numbers as shown) or from Exciton Chemical Co. (1a = C460, 1g = C485, 5 = C540A). Solutions of the dyes were photolyzed using either a 450 W Hanovia medium pressure Hg lamp, immersion well apparatus, and a Pyrex glass filter (>300 nm) or, for comparative runs, a Rayonet chamber reactor in which 13 x 150 mm Pyrex test tubes were irradiated.⁷ The samples were purged with nitrogen or argon except where noted. Since higher concentrations of dye led to more rapid disappearance (vide infra), relatively concentrated solutions were generally employed for product studies (10^{-2} - 10^{-3} M). Lengthy irradiation resulted in loss of dye which could be followed by uv-vis absorption or nuclear magnetic resonance (nmr) spectrometry. A general result was the deposition of a film which was difficult to characterize

(i.e., nmr analysis revealed mainly dye disappearance). However, small quantities of identifiable products were apparent from glc analysis (2m 10% OV-101 column, 200°) on photolysis of 1 in acetonitrile. Product 2a was identified by comparison of reported spectral data;⁶ the analogous 2b was obtained after column chromatography of the photoproduct (silica gel, 5% ethyl acetate - hexane eluent) followed by recrystallization from toluene: fine yellow crystals, mp 158-159°(10% isolated yield). Elemental analysis for C₁₂F₈H₁₀N₂O₂ was: 56.21 %C, 3.98 %H, and 5.40 %N (found); 56.04 %C, 3.92 %H, and 5.45 %N (theory). The spectral data consistent with structure 1b were as follows:

uv (methanol): $\lambda_{\text{max}} = 390 \text{ nm}$

ir (film): 3370, 2990, 1725, 1645, 1620, 1135, 1170, 1230
and 1300 cm^{-1}

nmr (CDCl₃): δ 7.40 (m, arom., 1H), 6.45 (m, arom. and
-CH), 4.40 (broad s, N-H), 3.28 (q, -CH₃, 2H),
and 1.20 (t, -CH₃, 3H)

Another product originating from 1a could not be isolated but was identified as 1 by glc - mass spectral analysis. The major ms peaks and assignments were as follows:

ms: m/e 233 (mol. ion), 218 (-CH₃), 190 (-CH₃, -CO or
C₂H₄), and 148 (190 - CH₃CO)

Although 2a and the previously unidentified 3 failed to accumulate appreciably with photolysis time (ca. 10% maximum), their appearance proved interesting in that 3 was favored at the shortest times possible for glc detection whereas 2a was the more important volatile component after lengthy irradiation periods. Confirming the rather erratic nature of photodegradation, the disappearance of native dye appeared to be accelerated following an induction period in which about 10% of the starting dye was decomposed. Glc analysis also revealed small quantities of the fully dealkylated dyes (identified by direct comparison with the commercially available C120 and C151 (4) from 2a' and 2b, respectively).

Coumarin 1c was also investigated to establish the dependence of photodealkylation on substitution at the amino group. The rate of decomposition in deaerated acetonitrile was in fact comparable to that of 1b and products of dealkylation were apparent from nmr and glc analysis (only the common product 4 was thoroughly identified). Photodecomposition of coumarins 1 as a function of solvent was followed by glc analysis of dealkylation product at relatively low conversion (anthracene used as an internal standard). Parallel irradiation showed similar results for acetonitrile, toluene, and cyclohexane with some acceleration in chloroform (ca. 3-fold) and a retardation in alcohols (>10-fold).

Photolysis of deaerated acetonitrile solutions of coumarin 153 (7) led to decomposition (significantly slower than 1) to intractable material with no appearance of an identifiable monomeric product. However, on photolysis of air-saturated solutions, a photoproduct was obtained after preparative thin-layer chromatography (Analtech 2000 μ silica gel (GF) plates, 3:2 hex-

ane - ethyl acetate eluent). The product ($R_f = 0.5$), a solid with reddish coloration recrystallized from methanol/water, mp 193-207°. Elemental analysis provided the following data: for $C_{16}F_3H_{13}NO_3$, %C, 59.38, %H, 3.75, %N, 4.29 (found); %C, 59.44, %H, 3.72, %N, 4.33 (theory). The spectral data were consistent with formation of a pair of photooxidation products, the isomeric amides, 1 and 2, which crystallized as a mixture.

uv (ethanol): λ_{max} 353 nm

ir (film): 1735, 1690, 1615, 1415, 1370, 1295, 1135 cm^{-1}

nmr (CDCl_3): δ 7.40 (s, arom., 1H), 6.70 (s, vinyl, 1H),
3.80 (m, N-CH₂, 2H), 2.80 (m, -CH₂, 2H),
1.1-2.2 (m, CH₂, 6H)

Mechanistic studies. For the purposes of establishing a mechanism of photodegradation, the effect of adding a triplet quencher was investigated. With 0.1 M 1,3-cyclohexadiene (CHD) or with 0.06 M *trans*-stilbene, neither formation of products, 2a and 3, nor the rate of net destruction of 1a was altered. As a control the quenching of dye triplets by these additives was investigated by flash photolysis. The triplet of 1a was observed (λ_{max} 625 nm) as previously reported⁸ on flash lamp irradiation in argon-purged acetonitrile (Xe source,⁹ pulse duration = ca. 30 μs FWHM). This transient was absent on the addition of triplet quenchers.

Although the quenching results for 1a did not favor a photolysis mechanism involving dye triplets, the appearance of triplets for other dyes

remained of interest. Intersystem crossing yields were measured for three dyes in two solvents using the triplet counting technique in which the photodimerization of CHD' via energy transfer from dye was followed with reference to dimerization sensitized by benzophenone (whose triplet yield (1.0) is known) (Table).¹¹

With a singlet mechanism for photodegradation in mind, dependences on dye concentration were investigated. In fact the appearance of β at low conversion (ca. 0.1%) was noticeably accelerated at high dye concentrations (0.01–0.25 M). The profile of concentration dependence is consistent with a singlet self-quenching mechanism according to Scheme 1. Along with values for singlet lifetime for 1_a in very dilute solution ($\tau = 1 / (k_p + k_d)$),¹¹ the data provide a source for the rate constant sum, $k_{eq} + k_r = 7.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ referring to the sum of rates for concentration quenching and bimolecular reaction. A similar value for these rates ($2.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) has been independently obtained by measuring the concentration quenching of fluorescence as reported separately for several coumarin dyes.¹² The plot of quantum yield data for formation of β (eqn 1) provided an estimate of the maximum (extrapolated) yield of product β , $(k_r + k_{eq})/k_r = 3 \times 10^{-4}$, which showed that the photoreduction of 1_a constitutes a small part of total (unproductive) concentration quenching.

Summary. The photodealkylation reaction for 7-dialkylaminocoumarins in deoxygenated media has been extended to fluorinated analogs, 1_b and 1_c . Another type of product, whose structure has been tentatively assigned to photoreduction product β , can be ascribed to formation of radicals δ and ϵ as previously proposed by von Trebra and Koch.¹² This type of intermediate

may arise from bimolecular quenching by ground state dye (self reaction of dye or concentration quenching) via rather inefficient hydrogen atom abstraction (or the equivalent steps of electron transfer and proton transfer). Radical 6 is capable of disproportionation to reduction product 3 and starting dye and the initiation of dye polymerization, whereas 5 is a likely intermediate for dealkylation either via coupling reaction with 6¹³ or by way of further electron/proton transfer.

The rigid coumarin, 1, is less photoactive in oxygen-free solutions than the analogs, 1, presumably due to low productivity in radical formation from its less energetic excited singlet (concentration quenching is nonetheless observed¹²). On the other hand, photoxidation in aerated solution is important. Formation of products 8 and 9 is consistent with the quenching of dye singlets by oxygen, a step which has been documented,^{11b,14} and formation of radicals (via hydrogen or electron/proton transfer). Photodecomposition proceeds as shown in Scheme 2 for reaction at a position adjacent to nitrogen, reminiscent of the path which has been proposed for oxidation of tertiary amines.¹⁵ The reaction observed for the amine functional group contrasts with the reported photooxidation of 1a⁶ (reaction at the 4-methyl group) and portends a more general destructive role for oxygen in the aminocoumarin series (a similar rate of degradation for a variety of coumarins under lasing conditions for air-saturated solutions has been reported.⁵

The results overall point to the importance of dye self quenching in photodegradation, a phenomenon which is alleviated but not entirely eliminated at low but practical dye concentrations. Alcohol (protic) solvents

reduce photodecomposition (but not concentration quenching¹³) presumably by inhibition of radical formation through hydrogen-bonding to the coumarin carbonyl group, a particularly effective interaction for the excited singlet dye.¹² The potential for destruction by oxygen in aerated samples is also reiterated.^{2, 8b, 6, 14} However, it should be noted that for the general case of laser dye stability the presence of oxygen is not necessarily defeating if there is a significant role for dye triplets in photodecomposition or in competitive absorption at lasing wavelengths.

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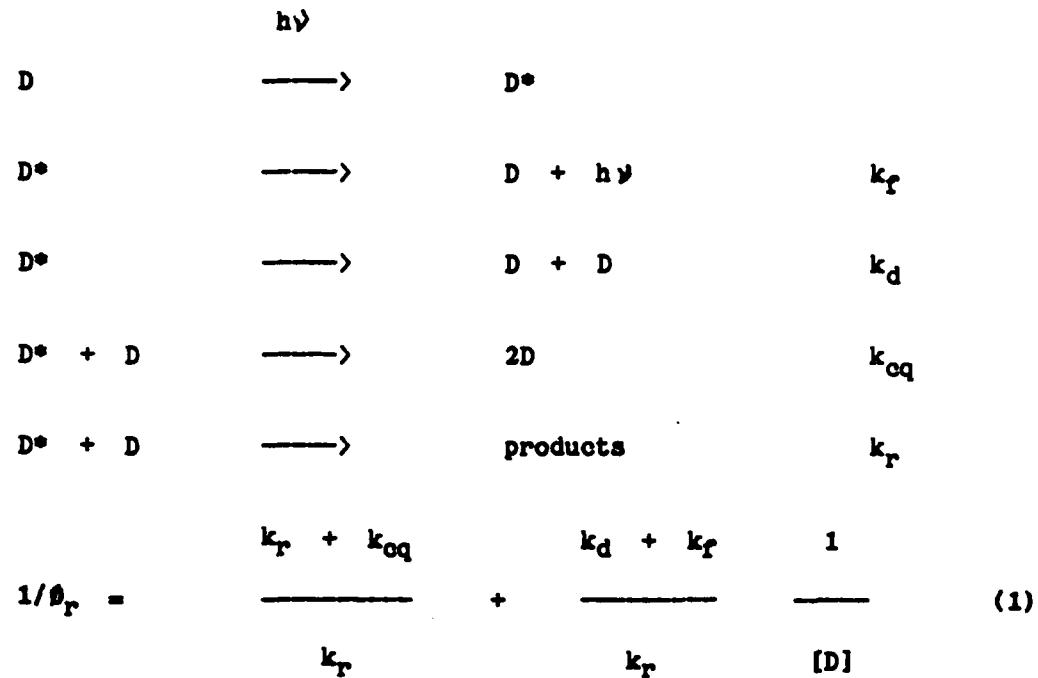
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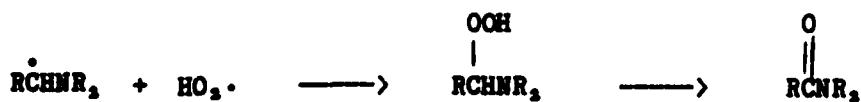
Table. Intersystem crossing quantum yields for coumarin dyes.

	$\theta_t(C_6H_{12})$	$\theta_t(C_2H_5OH)$
1a	0.30	0.006
1b	0.043	<0.001
1	0.053	<0.001

Scheme 1



Scheme 2



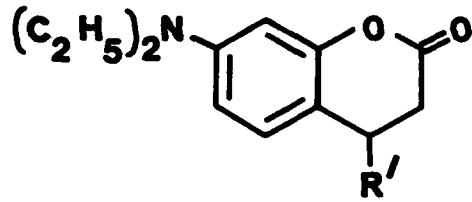


1a, R = C₂H₅, R' = CH₃ [C1]

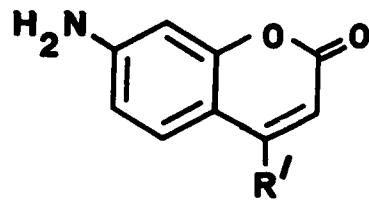
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1b, R = C₂H₅, R' = CF₃ [C35]

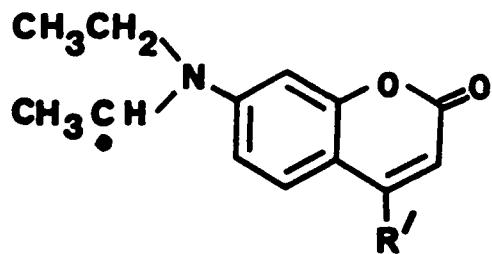
1c, R = CH₃, R' = CF₃ [C152]



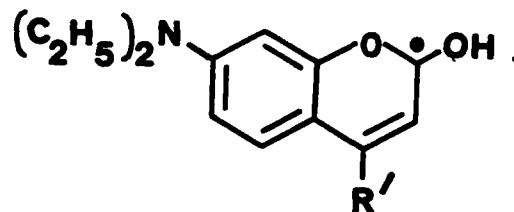
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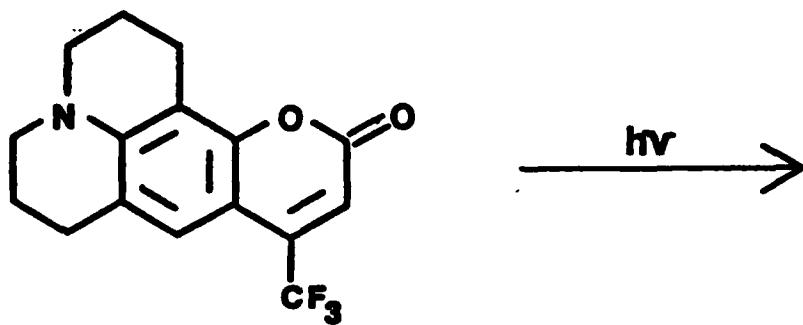
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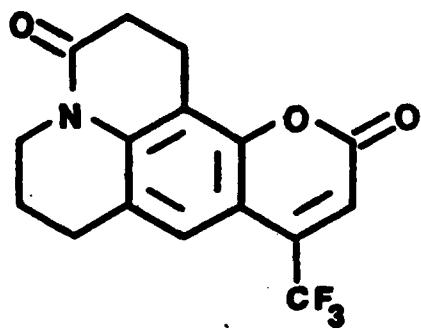
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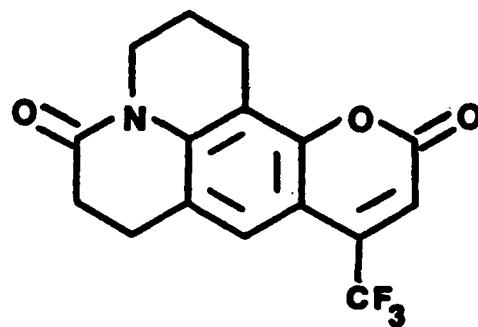
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7 (C153)



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